

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 206 794
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 86304806.2

(51) Int. Cl.: C 08 F 4/76, C 08 F 10/00

(22) Date of filing: 23.06.86

(30) Priority: 21.06.85 US 747615 85/747615

(71) Applicant: **EXXON CHEMICAL PATENTS INC.**, 200 Park Avenue, Florham Park New Jersey 07932 (US)(43) Date of publication of application: 30.12.86
Bulletin 86/52(72) Inventor: **Welborn, Howard Curtis, Jr.**, 1502 Driscoll Street, Houston Texas 77019 (US)(84) Designated Contracting States: **AT BE CH DE FR GB IT LI LU NL SE**(74) Representative: **Northover, Robert Frank et al, ESSO Chemical Limited Esso Chemical Research Centre P.O. Box 1, Abingdon Oxfordshire, OX13 6BB (GB)**

(54) Supported polymerization catalyst.

(57) An olefin polymerization supported catalyst comprising a support and the reaction product of a metallocene of Group 4b, 5b or 6b of the Periodic Table and an alumoxane, said reaction product formed in the presence of a support.

G. METALOCENOS

ARCHIVADO

REGISTRO DE LA PROPIEDAD INDUSTRIAL
Dpto. INFORMACION TECNOLÓGICA
Paseo 1 - Madrid 28011
Tel. (91) 453 22 00

EP 0 206 794 A1

SUPPORTED POLYMERIZATION CATALYST

1 This invention relates to a new, improved catalyst useful
2 for the polymerization and copolymerization of olefins and particu-
3 larly useful for the polymerization of ethylene and copolymerization
4 of ethylene with 1-olefins having 3 or more carbon atoms such as, for
5 example, propylene, i-butene, 1-butene, 1-pentene, 1-hexene, and
6 1-octene; dienes such as butadiene, 1,7-octadiene, and 1,4-hexadiene
7 or cyclic olefins such as norbornene. The invention particularly
8 relates to a new and improved heterogeneous transition metal contain-
9 ing supported catalyst which can be employed without the use of an
10 organometallic cocatalyst in the polymerization of olefins. The
11 invention further generally relates to a process for polymerization
12 of ethylene alone or with other 1-olefins or diolefins in the
13 presence of the new supported transition metal containing catalyst
14 comprising the reaction product of a metallocene and an alumoxane in
15 the presence of an support material such as silica.

Description of the Prior Art

17 Traditionally, ethylene and 1-olefins have been polymerized
18 or copolymerized in the presence of hydrocarbon insoluble catalyst
19 systems comprising a transition metal compound and an aluminum
20 alkyl. More recently, active homogeneous catalyst systems comprising
21 a bis(cyclopentadienyl)titanium dialkyl or a bis(cyclopentadienyl)-
22 zirconium dialkyl, an aluminum trialkyl and water have been found to
23 be useful for the polymerization of ethylene. Such catalyst systems
24 are generally referred to as "Ziegler-type catalysts".

25 DE-A-2608863 discloses the use of a
26 catalyst system for the polymerization of ethylene consisting of bis -
27 (cyclopentadienyl) titanium dialkyl, aluminum trialkyl and water.

28 DE-A-2608933 discloses an ethylene
29 polymerization catalyst system consisting of zirconium metallocenes
30 of the general formula $(\text{cyclopentadienyl})_n\text{ZrY}_{4-n}$, wherein n
31 stands for a number in the range of 1 to 4, Y for R, CH_2AlR_2 ,
32 $\text{CH}_2\text{CH}_2\text{AlR}_2$ and $\text{CH}_2\text{CH}(\text{AlR}_2)_2$, wherein R stands for alkyl or metallo
33 alkyl, and an aluminum trialkyl cocatalyst and water.

34 EP-A-0035242 discloses a process
35 for preparing ethylene and atactic propylene polymers in the presence
36 of a halogen-free Ziegler catalyst system of (1) cyclopentadienyl

1 compound of the formula (cyclopentadienyl)_nMeY_{4-n} in which n is an
2 integer from 1 to 4, Me is a transition metal, especially zirconium,
3 and Y is either hydrogen, a C₁-C₅ alkyl or metallo alkyl group or
4 a radical having the following general formula CH₂AlR₂, CH₂CH₂AlR₂ and
5 CH₂CH(AlR₂)₂ in which R represents a C₁-C₅ alkyl or metallo alkyl
6 group, and (2) an alumoxane.

7 Additional teachings of homogeneous catalyst systems com-
8 prising a metallocene and alumoxane are
9 EP-A-0069951, IJS 4404344 and EP-A-128045.

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12
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14 An advantage of the metallocene alumoxane homogeneous cata-
15 lyst system is the very high activity obtained for ethylene polymeri-
16 zation. Another significant advantage is, unlike olefin polymers
17 produced in the presence of conventional heterogeneous Ziegler cata-
18 lysts, terminal unsaturation is present in polymers produced in the
19 presence of these homogeneous catalysts. Nevertheless, the catalysts
20 suffer from a disadvantage, that is, the ratio of alumoxane to metal-
21 locene is high, for example in the order of 1,000 to 1 or greater.
22 Such voluminous amounts of alumoxane would require extensive treatment
23 of polymer product obtained in order to remove the undesirable alumi-
24 num. A second disadvantage, of the homogeneous catalyst system which
25 is also associated with traditional heterogeneous Ziegler catalysts,
26 is the multiple of delivery systems required for introducing the
27 individual catalyst components into the polymerization reactor.

28 It would be highly desirable to provide a metallocene based
29 catalyst which is commercially useful for the polymerization of ole-
30 fins wherein the aluminum to transition metal ratio is within respect-
31 able ranges and further to provide a polymerization catalyst which
32 does not require the presence of a cocatalyst thereby reducing the
33 number of delivery systems for introducing catalyst into polymeriza-
34 tion reactor.

1 Summary of the Invention

2 In accordance with the present invention, a new metallocene/
3 alumoxane catalyst is provided for olefin polymerization which cata-
4 lyst can be usefully employed for the production of low, medium and
5 high density polyethylenes and copolymers of ethylene with alpha-
6 olefins having 3 to 18 or more carbon atoms and/or diolefins having up
7 to 18 carbon atoms or more.

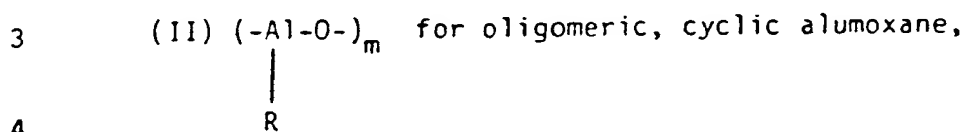
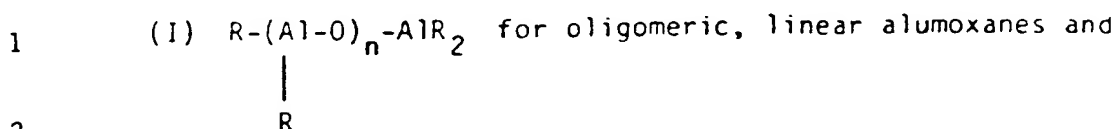
8 The new catalyst provided in accordance with one embodiment
9 of this invention, comprises the reaction product of at least one
10 metallocene and an alumoxane in the presence of an support material
11 thereby providing a supported metallocene-alumoxane reaction product
12 as the sole catalyst component.

13 The supported reaction product will polymerize olefins at
14 commercially respectable rates without the presence of the objection-
15 able excess of alumoxane as required in the homogenous system.

16 In yet another embodiment of this invention there is provided
17 a process for the polymerization of ethylene and other olefins, and
18 particularly homopolymers of ethylene and copolymers of ethylene and
19 higher alpha-olefins and/or diolefins and/or cyclic olefins such as
20 norbornene in the presence of the new catalysts.

21 The metallocenes employed in the production of the reaction
22 product on the support are organometallic coordination compounds which
23 are cyclopentadienyl derivatives of a Group 4b, 5b, or 6b metal of the
24 Periodic Table (56th Edition of Handbook of Chemistry and Physics, CRC
25 Press [1975]) and include mono, di and tricyclopentadienyls and their
26 derivatives of the transition metals. Particularly desirable are the
27 metallocene of a Group 4b and 5b metal such as titanium, zirconium,
28 hafnium and vanadium. The alumoxanes employed in forming the reaction
29 product with the metallocenes are themselves the reaction products of
30 an aluminum trialkyl with water.

31 The alumoxanes are well known in the art and preferably comprise oligo-
32 meric linear and/or cyclic alkyl alumoxanes represented by the formula:



5 wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R
 6 is a C_1-C_8 alkyl group and preferably methyl. Generally, in the
 7 preparation of alumoxanes from, for example, aluminum trimethyl and
 8 water, a mixture of linear and cyclic compounds is obtained.

9 The alumoxanes can be prepared in a variety of ways. Prefer-
 10 ably, they are prepared by contacting water with a solution of alumi-
 11 num trialkyl, such as, for example, aluminum trimethyl, in a suitable
 12 organic solvent such as benzene or an aliphatic hydrocarbon. For
 13 example, the aluminum alkyl is treated with water in the form of a
 14 moist solvent. In a preferred method, the aluminum alkyl, such as
 15 aluminum trimethyl, can be desirably contacted with a hydrated salt
 16 such as hydrated ferrous sulfate. The method comprises treating a
 17 dilute solution of aluminum trimethyl in, for example, toluene with
 18 ferrous sulfate heptahydrate.

19 PREFERRED EMBODIMENTS

20 Briefly, the transition metal containing catalyst of the
 21 present invention is obtained by reacting an alumoxane and a metal-
 22 locene in the presence of a solid support material. The supported
 23 reaction product can be employed as the sole catalyst component for
 24 the polymerization of olefins or, in the alternative, it can be
 25 employed with a organometallic cocatalyst.

26 Typically, the support can be any of the solid, particularly,
 27 porous supports such as talc, inorganic oxides, and resinous support
 28 materials such as polyolefin. Preferably, the support material is an
 29 inorganic oxide in finely divided form.

30 Suitable inorganic oxide materials which are desirably
 31 employed in accordance with this invention include Group 2a, 3a, 4a or
 32 4b metal oxides such as silica, alumina, and silica-alumina and mix-
 33 tures thereof. Other inorganic oxides that may be employed either
 34 alone or in combination with the silica, alumina or silica-alumina are

1 magnesia, titania, zirconia, and the like. Other suitable support
2 materials, however, can be employed, for example, finely divided
3 polyolefins such as finely divided polyethylene.

4 The metal oxides generally contain acidic surface hydroxyl
5 groups which will react with the alumoxane or transition metal com-
6 pound first added to the reaction solvent. Prior to use, the inorganic
7 oxide support may be dehydrated, ie subjected to a thermal treatment in
8 order to remove water and reduce the concentration of the surface
9 hydroxyl groups. The treatment may be carried out in vacuum or
10 while purging with a dry inert gas such as nitrogen at a temperature
11 of about 100°C to about 1000°C, and preferably, from about 300°C to
12 about 800°C. Pressure considerations are not critical. The duration
13 of the thermal treatment can be from about 1 to about 24 hours.
14 However, shorter or longer times can be employed provided equilibrium
15 is established with the surface hydroxyl groups.

16 Chemical dehydration as an alternative method of dehydration
17 of the metal oxide support material can advantageously be employed.
18 Chemical dehydration converts all water and hydroxyl groups on the
19 oxide surface to inert species. Useful chemical agents are for
20 example, SiCl_4 ; chlorosilanes, such as trimethylchlorosilane,
21 dimethyaminotrimethylsilane and the like. The chemical dehydration is
22 accomplished by slurrying the inorganic particulate material, such as,
23 for example, silica in an inert low boiling hydrocarbon, such as, for
24 example, hexane. During the chemical dehydration reaction, the silica
25 should be maintained in a moisture and oxygen-free atmosphere. To the
26 silica slurry is then added a low boiling inert hydrocarbon solution
27 of the chemical dehydrating agent, such as, for example, dichlorodi-
28 methylsilane. The solution is added slowly to the slurry. The
29 temperature ranges during chemical dehydration reaction can be from
30 about 25°C to about 120°C, however, higher and lower temperatures can
31 be employed. Preferably, the temperature will be about 50°C to about
32 70°C. The chemical dehydration procedure should be allowed to proceed
33 until all the moisture is removed from the particulate support
34 material, as indicated by cessation of gas evolution. Normally, the
35 chemical dehydration reaction will be allowed to proceed from about 30
36 minutes to about 16 hours, preferably 1 to 5 hours. Upon completion
37 of the chemical dehydration, the solid particulate material is
38 filtered under a nitrogen atmosphere and washed one or more times

1 with a dry, oxygen-free inert hydrocarbon solvent. The wash solvents,
2 as well as the diluents employed to form the slurry and the solution
3 of chemical dehydrating agent, can be any suitable inert hydrocarbon.
4 Illustrative of such hydrocarbons are heptane, hexane, toluene, iso-
5 pentane and the like.

6 The normally hydrocarbon soluble metallocenes and alumoxanes
7 are converted to a heterogeneous supported catalyst by depositing said
8 metallocenes and alumoxanes on the dehydrated support material. The
9 order of addition of the metallocene and alumoxane to the support
10 material can vary. For example, the metallocene (neat or dissolved in
11 a suitable hydrocarbon solvent) can be first added to the support
12 material followed by the addition of the alumoxane; the alumoxane and
13 metallocene can be added to the support material simultaneously; the
14 alumoxane can be first added to the support material followed by the
15 addition of the metallocene. In accordance with the preferred embodi-
16 ment of this invention the alumoxane dissolved in a suitable inert
17 hydrocarbon solvent is added to the support material slurried in the
18 same or other suitable hydrocarbon liquid and thereafter the metal-
19 locene is added to the slurry.

20 The treatment of the support material, as mentioned above, is
21 conducted in an inert solvent. The same inert solvent or a different
22 inert solvent is also employed to dissolve the metallocenes and alum-
23 oxanes. Preferred solvents include mineral oils and the various
24 hydrocarbons which are liquid at reaction temperatures and in which
25 the individual ingredients are soluble. Illustrative examples of
26 useful solvents include the alkanes such as pentane, iso-pentane,
27 hexane, heptane, octane and nonane; cycloalkanes such as cyclopentane
28 and cyclohexane; and aromatics such as benzene, toluene, ethylbenzene
29 and diethylbenzene. Preferably the support material is slurried in
30 toluene and the metallocene and alumoxane are dissolved in toluene
31 prior to addition to the support material. The amount of solvent to
32 be employed is not critical. Nevertheless, the amount should be
33 employed so as to provide adequate heat transfer away from the cata-
34 lyst components during reaction and to permit good mixing.

35 The supported catalyst of this invention is prepared by
36 simply adding the reactants in the suitable solvent and preferably
37 toluene to the support material slurry, preferably silica slurried in
38 toluene. The ingredients can be added to the reaction vessel rapidly

1 or slowly. The temperature maintained during the contact of the
2 reactants can vary widely, such as, for example, from 0° to 100°C.
3 Greater or lesser temperatures can also be employed. Preferably, the
4 alumoxanes and metallocenes are added to the silica at room tempera-
5 ture. The reaction between the alumoxane and the support material is
6 rapid, however, it is desirable that the alumoxane be contacted with
7 the support material for about one hour up to eighteen hours or
8 greater. Preferably, the reaction is maintained for about one hour.
9 The reaction of the alumoxane, the metallocene and the support
10 material is evidenced by its exothermic nature and a color change.

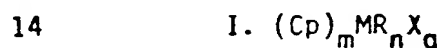
11 At all times, the individual ingredients as well as the
12 recovered catalyst component are protected from oxygen and moisture.
13 Therefore, the reactions must be performed in an oxygen and moisture
14 free atmosphere and recovered in an oxygen and moisture free atmos-
15 phere. Preferably, therefore, the reactions are performed in the
16 presence of an inert dry gas such as, for example, nitrogen. The
17 recovered solid catalyst is maintained in a nitrogen atmosphere.

18 Upon completion of the reaction of the metallocene and alum-
19 oxane with the support, the solid material can be recovered by any
20 well-known technique. For example, the solid material can be recov-
21 ered from the liquid by vacuum evaporation or decantation. The solid
22 is thereafter dried under a stream of pure dry nitrogen or dried under
23 vacuum.

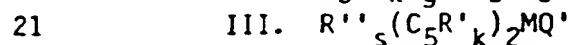
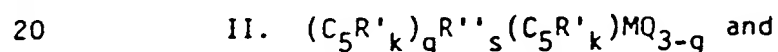
24 The amount of alumoxane and metallocene usefully employed in
25 preparation of the solid supported catalyst component can vary over a
26 wide range. The concentration of the alumoxane added to the essen-
27 tially dry, support can be in the range of about 0.1 to about 10
28 mmols/g of support, however, greater or lesser amounts can be use-
29 fully employed. Preferably, the alumoxane concentration will be in
30 the range of 0.5 to 10 mmols/g of support and especially 1 to 5
31 mmols/g of support. The amount of metallocene added will be such as
32 to provide an aluminum to transition metal mole ratio of from about
33 1:1 to about 100:1. Preferably, the ratio is in the range from about
34 5:1 to about 50:1 and more preferably in the range from about 10:1 to
35 about 20:1. These ratios are significantly less than that which is
36 necessary for the homogeneous system.

1 The present invention employs at least one metallocene com-
 2 pound in the formation of the supported catalyst. Metallocene, i.e. a
 3 cyclopentadienylide, is a metal derivative of a cyclopentadiene. The
 4 metallocenes usefully employed in accordance with this invention
 5 contain at least one cyclopentadiene ring. The metal is selected from
 6 Group 4b, 5b and 6b metal, preferably 4b and 5b metals, preferably
 7 titanium, zirconium, hafnium, chromium, and vanadium, and especially
 8 titanium and zirconium. The cyclopentadienyl ring can be unsubsti-
 9 tuted or contain substituents such as, for example, a hydrocarbyl
 10 substituent. The metallocene can contain one, two, or three cyclo-
 11 pentadienyl ring however two rings are preferred.

12 The preferred metallocenes can be represented by the general
 13 formulas:



15 wherein Cp is a cyclopentadienyl ring, M is a Group 4b, 5b, or 6b
 16 transition metal, R is a hydrocarbyl group or hydrocarboxy having from
 17 1 to 20 carbon atoms, X is a halogen, and $m = 1-3$, $n = 0-3$, $q = 0-3$
 18 and the sum of $m+n+q$ will be equal to the oxidation state of the
 19 metal.



22 wherein $(C_5R'_k)$ is a cyclopentadienyl or substituted cyclopenta-
 23 dienyl, each R' is the same or different and is hydrogen or a hydro-
 24 carbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl
 25 radical containing from 1 to 20 carbon atoms or two carbon atoms are
 26 joined together to form a C_4-C_6 ring, R'' is a C_1-C_4 alkylene
 27 radical, a dialkyl germanium or silicon, or a alkyl phosphine or amine
 28 radical bridging two $(C_5R'_k)$ rings, Q is a hydrocarbyl radical
 29 such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having
 30 from 1-20 carbon atoms, hydrocarboxy radical having from 1-20 carbon
 31 atoms or halogen and can be the same or different from each other, Q'
 32 is an alkylidene radical having from 1 to about 20 carbon atoms, s is
 33 0 or 1, g is 0, 1 or 2, s is 0 when g is 0, k is 4 when s is 1 and k
 34 is 5 when s is 0, and M is as defined above.

35 Exemplary hydrocarbyl radicals are methyl, ethyl, propyl,
 36 butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl,
 37 cetyl, 2-ethylhexyl, phenyl and the like.

1 Exemplary halogen atoms include chlorine, bromine, fluorine
2 and iodine and of these halogen atoms, chlorine is preferred.

3 Exemplary hydrocarboxy radicals are methoxy, ethoxy, propoxy,
4 butoxy, amyloxy and the like.

5 Exemplary of the alkylidene radicals is methylidene, ethyli-
6 dene and propylidene.

7 Illustrative, but non-limiting examples of the metallocenes
8 represented by formula I are dialkyl metallocenes such as bis(cyclo-
9 pentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium diphenyl,
10 bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)-
11 zirconium diphenyl, bis(cyclopentadienyl)hafnium dimethyl and
12 diphenyl, bis(cyclopentadienyl)titanium di-neopentyl, bis(cyclopenta-
13 dienyl)zirconium di-neopentyl, bis(cyclopentadienyl)titanium dibenzyl,
14 bis(cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl)vanadium
15 dimethyl; the mono alkyl metallocenes such as bis(cyclopentadienyl)-
16 titanium methyl chloride, bis(cyclopentadienyl)titanium ethyl
17 chloride, bis(cyclopentadienyl)titanium phenyl chloride, bis(cyclo-
18 pentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium
19 ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride, bis-
20 (cyclopentadienyl)titanium methyl bromide, bis(cyclopentadienyl)methyl
21 iodide, bis(cyclopentadienyl)titanium ethyl bromide, bis(cyclopenta-
22 dienyl)titanium ethyl iodide, bis(cyclopentadienyl)titanium phenyl
23 bromide, bis(cyclopentadienyl)titanium phenyl iodide, bis(cyclopenta-
24 dienyl)zirconium methyl bromide, bis(cyclopentadienyl)zirconium methyl
25 iodide, bis(cyclopentadienyl)zirconium ethyl bromide, bis(cyclopenta-
26 dienyl)zirconium ethyl iodide, bis(cyclopentadienyl)zirconium phenyl
27 bromide, bis(cyclopentadienyl)zirconium phenyl iodide; the trialkyl
28 metallocenes such as cyclopentadienyltitanium trimethyl, cyclopenta-
29 dienyl zirconium triphenyl, and cyclopentadienyl zirconium trineo-
30 pentyl, cyclopentadienylzirconium trimethyl, cyclopentadienylhafnium
31 triphenyl, cyclopentadienylhafnium trineopentyl, and cyclopentadienyl-
32 hafnium trimethyl.

33 Illustrative, but non-limiting examples of II and III metal-
34 locenes which can be usefully employed in accordance with this inven-
35 tion are monocyclopentadienyls titanocenes such as, pentamethylcyclo-
36 pentadienyl titanium trichloride, pentaethylcyclopentadienyl titanium
37 trichloride; bis(pentamethylcyclopentadienyl) titanium diphenyl, the
38 carbene represented by the formula bis(cyclopentadienyl)titanium=CH₂

1 and derivatives of this reagent such as bis(cyclopentadienyl)-
 2 $\text{Ti}=\text{CH}_2\text{-Al}(\text{CH}_3)_3$, $(\text{Cp}_2\text{TiCH}_2)_2$, $\text{Cp}_2\text{TiCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$,
 3 $\text{Cp}_2\text{Ti-CHCH}_2\text{CH}_2$; substituted bis(cyclopentadienyl)titanium (IV)
 4 compounds such as: bis(indenyl)titanium diphenyl or dichloride, bis-
 5 (methylcyclopentadienyl)titanium diphenyl or dihalides; dialkyl,
 6 trialkyl; tetra-alkyl and penta-alkyl cyclopentadienyl titanium
 7 compounds such as bis(1,2-dimethylcyclopentadienyl)titanium diphenyl
 8 or dichloride, bis(1,2-diethylcyclopentadienyl)titanium diphenyl or
 9 dichloride and other dihalide complexes; silicon, phosphine, amine or
 10 carbon bridged cyclopentadiene complexes, such as dimethyl silyl-
 11 dicyclopentadienyl titanium diphenyl or dichloride, methyl phosphine
 12 dicyclopentadienyl titanium diphenyl or dichloride, methylenedi-
 13 cyclopentadienyl titanium diphenyl or dichloride and other dihalide
 14 complexes and the like.

15 Illustrative but non-limiting examples of the zirconocenes
 16 Formula II and III which can be usefully employed in accordance with
 17 this invention are, pentamethylcyclopentadienyl zirconium trichloride,
 18 pentaethylcyclopentadienyl zirconium trichloride, bis(pentamethyl-
 19 cyclopentadienyl)zirconium diphenyl, the alkyl substituted cyclopenta-
 20 dienes, such as bis(ethyl cyclopentadienyl)zirconium dimethyl, bis-
 21 (β -phenylpropylcyclopentadienyl)zirconium dimethyl, bis(methylcyclo-
 22 pentadienyl)zirconium dimethyl, bis(n-butyl-cyclopentadienyl)zirconium
 23 dimethyl, bis(cyclohexylmethylcyclopentadienyl)zirconium dimethyl,
 24 bis(n-octyl-cyclopentadienyl)zirconium dimethyl, and haloalkyl and
 25 dihalide complexes of the above; di-alkyl, trialkyl, tetra-alkyl, and
 26 penta-alkyl cyclopentadienes, such as bis(pentamethylcyclopentadienyl)
 27 zirconium di-methyl, bis(1,2-dimethylcyclopentadienyl)zirconium
 28 dimethyl and dihalide complexes of the above; silicone, phosphorus,
 29 and carbon bridged cyclopentadiene complexes such as dimethylsilyldi-
 30 cyclopentadienyl zirconium dimethyl or dihalide, and methylene
 31 dicyclopentadienyl zirconium dimethyl or dihalide, and methylene
 32 dicyclopentadienyl zirconium dimethyl or dihalide, carbenes
 33 represented by the formula $\text{Cp}_2\text{Zr}=\text{CHP}(\text{C}_6\text{H}_5)_2\text{CH}_3$, and derivatives of these
 34 compounds such as $\text{Cp}_2\text{ZrCH}_2\text{CH}(\text{CH}_3)\text{CH}_2$.

35 Bis(cyclopentadienyl)hafnium dichloride, bis(cyclopenta-
 36 dienyl)hafnium dimethyl, bis(cyclopentadienyl)vanadium dichloride and
 37 the like are illustrative of other metallocenes.

1 The inorganic oxide support used in the preparation of the
2 catalyst may be any particulate oxide or mixed oxide as previously
3 described which has been thermally or chemically dehydrated such that
4 it is substantially free of adsorbed moisture.

5 The specific particle size, surface area, pore volume, and
6 number of surface hydroxyl groups characteristic of the inorganic
7 oxide are not critical to its utility in the practice of the inven-
8 tion. However, since such characteristics determine the amount of
9 inorganic oxide that it is desirable to employ in preparing the cata-
10 lyst compositions, as well as affecting the properties of polymers
11 formed with the aid of the catalyst compositions, these character-
12 istics must frequently be taken into consideration in choosing an
13 inorganic oxide for use in a particular aspect of the invention. For
14 example, when the catalyst composition is to be used in a gas-phase
15 polymerization process - a type of process in which it is known that
16 the polymer particle size can be varied by varying the particle size
17 of the support - the inorganic oxide used in preparing the catalyst
18 composition should be one having a particle size that is suitable for
19 the production of a polymer having the desired particle size. In
20 general, optimum results are usually obtained by the use of inorganic
21 oxides having an average particle size in the range of about 30 to 600
22 microns, preferably about 30 to 100 microns; a surface area of about
23 50 to 1,000 square meters per gram, preferably about 100 to 400 square
24 meters per gram; and a pore volume of about 0.5 to 3.5 cc per gram;
25 preferably about 0.5 to 2cc per gram.

26 The polymerization may be conducted by a solution, slurry, or
27 gas-phase technique, generally at a temperature in the range of about
28 0°-160°C or even higher, and under atmospheric, subatmospheric, or
29 superatmospheric pressure conditions; and conventional polymerization
30 adjuvants, such as hydrogen may be employed if desired. It is
31 generally preferred to use the catalyst compositions at a concentra-
32 tion such as to provide about 0.000001 - 0.005%, most preferably about
33 0.00001 - 0.0003%, by weight of transition metal based on the weight
34 of monomer(s), in the polymerization of ethylene, alone or with one or
35 more higher olefins.

36 A slurry polymerization process can utilize sub-atmospheric
37 atmospheric pressures and temperatures in the range of 40-110°
38 slurry polymerization, a suspension of solid, particulate catalyst

1 is formed in a liquid polymerization medium to which ethylene, alpha-
2 olefin comonomer, hydrogen and catalyst are added. The liquid
3 employed as the polymerization medium can be an alkane or cycloalkane,
4 such as butane, pentane, hexane, or cyclohexane, or an aromatic hydro-
5 carbon, such as toluene, ethylbenzene or xylene. The medium employed
6 should be liquid under the conditions of the polymerization and rela-
7 tively inert. Preferably, hexane or toluene is employed.

8 A gas-phase polymerization process utilizes superatmospheric
9 pressure and temperatures in the range of about 50°-120°C. Gas-phase
10 polymerization can be performed in a stirred or fluidized bed of
11 catalyst and product particles in a pressure vessel adapted to permit
12 the separation of product particles from unreacted gases. Thermo-
13 stated ethylene, comonomer, hydrogen and an inert diluent gas such as
14 nitrogen can be introduced or recirculated so as to maintain the
15 particles at a temperature of 50°-120°C. Triethylaluminum may be
16 added as needed as a scavenger of water, oxygen, and other adventi-
17 tious impurities. Polymer product can be withdrawn continuously or
18 semi-continuing at a rate such as to maintain a constant product
19 inventory in the reactor. After polymerization and deactivation of
20 the catalyst, the product polymer can be recovered by any suitable
21 means. In commercial practice, the polymer product can be recovered
22 directly from the gas phase reactor, freed of residual monomer with a
23 nitrogen purge, and used without further deactivation or catalyst
24 removal. The polymer obtained can be extruded into water and cut into
25 pellets or other suitable comminuted shapes. Pigments, antioxidants
26 and other additives, as is known in the art, may be added to the
27 polymer.

28 The molecular weight of polymer product obtained in accor-
29 dance with this invention can vary over a wide range, such as low as
30 500 up to 2,000,000 or higher and preferably 1,000 to about 500,000.

31 For the production of polymer product having a narrow molecu-
32 lar weight distribution, it is preferable to deposit only one metal-
33 locene on to the inert porous support material and employ said support
34 metallocene together with the alumoxane as the polymerization cata-
35 lyst.

→ 1 It is highly desirable to have for many applications, such as
2 extrusion and molding processes, polyethylenes which have a broad
3 molecular weight distribution of the unimodal and/or the multimodal
4 type. Such polyethylenes evidence excellent processability, i.e. they
5 can be processed at a faster throughput rate with lower energy
6 requirements and at the same time such polymers would evidence reduced
7 melt flow perturbations. Such polyethylenes can be obtained by pro-
8 viding a catalyst component comprising at least two different metal-
9 locenes, each having different propagation and termination rate con-
- 10 ~~stants~~ for ethylene polymerizations. Such rate constants are readily
11 determined by one of ordinary skill in the art.

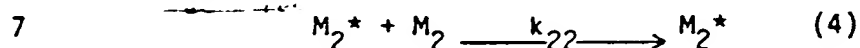
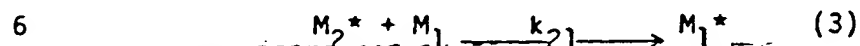
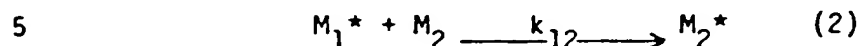
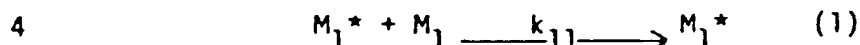
12 • The molar ratio of the metallocenes, such as, for example, of
13 a zirconocene to a titanocene in such catalysts, can vary over a wide
14 range, and in accordance with this invention, the only limitation on
15 the molar ratios is the breadth of the Mw distribution or the degree
16 of bimodality desired in the product polymer. Desirably, the metal-
17 locene to metallocene molar ratio will be about 1:100 to about 100:1,
18 and preferably 1:10 to about 10:1.

→ 19 The present invention also provides a process for producing
20 (co)polyolefin reactor blends comprising polyethylene and copoly-
21 ethylene-alpha-olefins. The reactor blends are obtained directly
22 during a single polymerization process, i.e., the blends of this
23 invention are obtained in a single reactor by simultaneously poly-
24 merizing ethylene and copolymerizing ethylene with an alpha-olefin
25 thereby eliminating expensive blending operations. The process of
26 producing reactor blends in accordance with this invention can be
27 employed in conjunction with other prior art blending techniques, for
28 example, the reactor blends produced in a first reactor can be sub-
29 jected to further blending in a second stage by use of the series
30 reactors.

→ 31 In order to produce reactor blends the supported metallocene
32 catalyst component comprises at least two different metallocenes each
33 having different comonomer reactivity ratios.

→ 34 The comonomer reactivity ratios of the metallocenes in
35 general are obtained by well known methods, such as for example, as
36 described in "Linear Method for Determining Monomer Reactivity Ratios
37 in Copolymerization", M. Fineman and S. D. Ross, J. Polymer Science 5,
38 259 (1950) or "Copolymerization", F. R. Mayo and C. Walling, Chem.

1 Rev. 46, 191 (1950) incorporated herein in its entirety by reference.
 2 For example, to determine reactivity ratios the most widely used
 3 copolymerization model is based on the following equations:



8 where M_i refers to a monomer molecule which is arbitrarily design-
 9 nated i (where $i = 1, 2$) and M_i^* refers to a growing polymer chain
 10 to which monomer i has most recently attached.

11 The k_{ij} values are the rate constants for the indicated
 12 reactions. In this case, k_{11} represents the rate at which an ethy-
 13 lene unit inserts into a growing polymer chain in which the previously
 14 inserted monomer unit was also ethylene. The reactivity rates follow
 15 as: $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$

16 wherein k_{11} , k_{12} , k_{22} and k_{21} are the rate constants for
 17 ethylene (1) or comonomer (2) addition to a catalyst site where the
 18 last polymerized monomer is ethylene (k_{1x}) or comonomer (2) (k_{2x}).

19 Since, in accordance with this invention, one can produce high
 20 viscosity polymer product at a relatively high temperature, tempera-
 21 ture does not constitute a limiting parameter as with the prior art
 22 metallocene/alumoxane catalyst. The catalyst systems described
 23 herein, therefore, are suitable for the polymerization of olefins in
 24 solution, slurry or gas phase polymerizations and over a wide range of
 25 temperatures and pressures. For example, such temperatures may be in
 26 the range of about -60°C to about 280°C and especially in the range of
 27 about 0°C to about 160°C . The pressures employed in the process of
 28 the present invention are those well known, for example, in the range
 29 or about 1 to 500 atmospheres, however, higher pressures can be
 30 employed.

31 The polymers produced by the process of this present inven-
 32 tion are capable of being fabricated into a wide variety of articles,
 33 as is known for homopolymers of ethylene and copolymers of ethylene
 34 and higher alpha-olefins.

1 In a slurry phase polymerization, the alkyl aluminum scav-
2 enger is preferably dissolved in a suitable solvent, typically in an
3 inert hydrocarbon solvent such as toluene, xylene, and the like in a
4 molar concentration of about $5 \times 10^{-3} M$. However, greater or lesser
5 amounts can be used.

6 The present invention is illustrated by the following ex-
7 amples.

8 Examples

9 In the Examples following the alumoxane employed was prepared
10 by adding 76.5 grams ferrous sulfate heptahydrate in 4 equally spaced
11 increments over a 2 hour period to a rapidly stirred 2 liter round-
12 bottom flask containing 1 liter of a 13.1 wt. % solution of trimethyl-
13 aluminum (TMA) in toluene. The flask was maintained at 50°C and under
14 a nitrogen atmosphere. Methane produced was continuously vented.
15 Upon completion of the addition of ferrous sulfate heptahydrate the
16 flask was continuously stirred and maintained at a temperature of 50°C
17 for 6 hours. The reaction mixture was cooled to room temperature and
18 was allowed to settle. The clear solution containing the alumoxane
19 was separated by decantation from the insoluble solids.

20 Molecular weights were determined on a Waters Associates
21 Model No. 150C GPC (Gel Permeation Chromatography). The measurements
22 were obtained by dissolving polymer samples in hot trichlorobenzene
23 and filtered. The GPC runs are performed at 145°C in trichlorobenzene
24 at 1.0 ml/min flow using styragel columns from Perkin Elmer, Inc.
25 3.1% solutions (300 microliters of trichlorobenzene solution) were
26 injected and the samples were run in duplicate. The integration
27 parameters were obtained with a Hewlett-Packard Data Module.

28 Catalyst Preparation

29 Catalyst A

30 10 grams of a high surface area (Davison 952) silica, dehy-
31 drated in a flow of dry nitrogen at 800°C for 5 hours, was slurried
32 with 50 cc of toluene at 25°C under nitrogen in a 250 cc round-bottom
33 flask using a magnetic stirrer. 25 cc of methyl alumoxane in toluene
34 (1.03 moles/liter in aluminum) was added dropwise over 5 minutes with
35 constant stirring to the silica slurry. Stirring was continued for 30
36 minutes while maintaining the temperature at 25°C at which time the
37 toluene was decanted off and the solids recovered. To the alumoxane
38 treated silica was added dropwise over 5 minutes, with constant

1 stirring 25.0 cc of a toluene solution containing 0.200 gram of dicy-
2 clopentadienyl zirconium dichloride. The slurry was stirred an addi-
3 tional 1/2 hour while maintaining the temperature at 25°C and there-
4 after the toluene was decanted and the solids recovered and dried in
5 vacuo for 4 hours. The recovered solid was neither soluble nor
6 extractable in hexane. Analysis of the catalyst indicated that it
7 contained 4.5 wt. % aluminum and 0.63 wt. % zirconium.

8 Catalyst B

9 This catalyst will demonstrate that the use of the catalyst
10 of this invention in the production of copolyethylene with 1-butene
11 results in the more efficient incorporation of 1-butene as demon-
12 strated by the polymer product density.

13 The procedure for the preparation of Catalyst A was followed
14 with the exception that the methylalumoxane treatment of the support
15 material was eliminated. Analysis of the recovered solid indicated
16 that it contained 0.63 wt. % zirconium and 0 wt. % aluminum.

17 Catalyst C

18 The procedure for the preparation of Catalyst A was followed
19 except that 0.300 of bis(cyclopentadienyl) zirconium dimethyl was
20 substituted for the bis(cyclopentadienyl) zirconium dichloride.
21 Analysis of the recovered solid indicated that it contained 4.2 wt. %
22 aluminum and 1.1 wt. % zirconium.

23 Catalyst D

24 The procedure for preparation of Catalyst A was followed with
25 the exception that 0.270 g of bis(n-butyl-cyclopentadienyl) zirconium
26 dichloride was substituted for the bis(cyclopentadienyl) zirconium
27 dichloride of Catalyst A and all procedures were performed at 80°C.
28 Analysis of the recovered solids indicated that it contained 0.61 wt.
29 % zirconium and 4.3 wt. % aluminum.

30 Catalyst E

31 The procedure for preparation of Catalyst D was followed with
32 the exception that 0.250 grams of bis(n-butyl-cyclopentadienyl)-
33 zirconium dimethyl was substituted for the metallocene dichloride.
34 Analysis of the recovered solid indicated that it contained 0.63 wt %
35 zirconium and 4.2 wt % aluminum.

1 Catalyst F

2 The procedure for the preparation of Catalyst D was followed
3 with the exception that .500 grams of bis(pentamethylcyclopenta-
4 dienyl)zirconium dichloride was substituted for the metallocene.
5 Analysis of the recovered solid indicated that it contained 0.65 wt %
6 zirconium and 4.7 wt % aluminum.

7 Example 1 - Polymerization - Catalyst A

8 Polymerization performed in the gas phase in a 1-liter auto-
9 clave reactor equipped with a paddle stirrer, an external water jacket
10 for temperature control, a septum inlet and a regulated supply of dry
11 nitrogen, ethylene, hydrogen and 1-butene. The reactor, containing
12 40.0 g of ground polystyrene (10 mesh) which was added to aid stirring
13 in the gas phase, was dried and degassed thoroughly at 85°C. As a
14 scavenger, 2.00 cc of a methyl alumoxane solution (0.64 molar in total
15 aluminum) was injected through the septum inlet, into the vessel using
16 a gas-tight syringe in order to remove traces of oxygen and water.
17 The reactor contents were stirred at 120 rpm at 85°C for 1 minute at 0
18 psig nitrogen pressure. 500.0 mg of Catalyst A was injected into the
19 reactor and the reactor was pressured to 200 psig with ethylene. The
20 polymerization was continued for 10 minutes while maintaining the
21 reaction vessel at 85°C and 200 psig by constant ethylene flow. The
22 reaction was stopped by rapidly cooling and venting. 12.3 grams of
23 polyethylene were recovered. The polyethylene was recovered by
24 stirring the product with 1 liter of dichloromethane at 40°C, filter-
25 ing and washing with dichloromethane to recover the insoluble poly-
26 ethylene product from the soluble polystyrene stirring aid. The
27 polyethylene had a molecular weight of 146,000.

28 Example 2 - Polymerization - Catalyst A

29 Polymerization was performed as in Example 1 in the presence
30 of Catalyst A except that 3.0 psig of hydrogen was pressured into the
31 reactor prior to ethylene injection. 13.2 grams of polyethylene were
32 recovered having a molecular weight of 29,000.

33 Example 3 - Polymerization - Catalyst A

34 Polymerization was performed as in Example 1 in the presence
35 of Catalyst A except that 13.0 cc (0.137 moles) of 1-butene was
36 pressured into the reactor together with the ethylene after the
37 catalyst injection. 13.8 grams of polyethylene were recovered having
38 a molecular weight of 39,000 and a density of 0.918 g/cc.

1 Comparative Example 3A - Polymerization - Catalyst B

2 The polymerization was performed as in Example 1 with the
3 exception that Catalyst B was substituted for Catalyst A. 17.3 g of
4 polyethylene were recovered having a molecular weight of 67,000 and a
5 density of 0.935 g/cc. The higher density as compared with that
6 obtained in Example 3 demonstrates the less efficient incorporation of
7 comonomer.

8 Example 4 - Polymerization - Catalyst C

9 Polymerization was performed as in Example 1 with the excep-
10 tion that Catalyst C was used in place of Catalyst A. 9.8 grams of
11 polyethylene were recovered having a molecular weight of 189,000 and a
12 density of 0.960 g/cc.

13 Example 5 - Polymerization - Catalyst C

14 Polymerization was performed as in Example 4 except that 13.0
15 cc of 1-butene (0.123 moles) and 0.6 psig of hydrogen (1.66 milli-
16 moles) was introduced after the catalyst together with the ethylene.
17 6.5 grams of polyethylene were recovered having a molecular weight of
18 41,000 and a density of 0.926 g/cc.

19 Example 6 - Polymerization - Catalyst C

20 Polymerization was performed as in Example 4, except that the
21 scavenger methyl alumoxane was eliminated and no other aluminumalkyl
22 scavenger was injected. 10.2 grams of polyethene was recovered having
23 a molecular weight of 120,000 and a density of 0.960 g/cc.

24 Example 7 - Polymerization - Catalyst D

25 Polymerization was performed as in Example 1 with the excep-
26 tion that 0.6 cc of a 25 wt. % triethylaluminum in hexane was substi-
27 tuted for the methylalumoxane solution of Example 1, and Catalyst D
28 was employed in place of Catalyst A. 50.4 g of polyethylene was
29 recovered having a molecular weight of 196,000 and a density of 0.958
30 g/cc.

31 Example 8 - Polymerization - Catalyst D

32 Polymerization was performed as in Example 1 with the excep-
33 tion that the scavenger, methylalumoxane was eliminated, Catalyst D
34 was employed in place of Catalyst A and the polymerization was stopped
35 at the end of 5 minutes. 28.8 g of polyethylene was recovered having
36 a molecular weight of 196,000 and a density of 0.958 g/cc.

1 Example 9 - Polymerization - Catalyst E

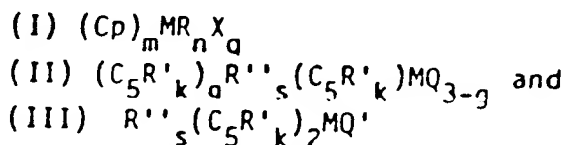
2 Polymerization was performed as in Example 8 using Catalyst E
3 with no scavenger aluminum compound. 24.0 grams of polyethylene was
4 recovered having a weight average molecular weight of 190,000, a
5 number average molecular weight of 76,000 and a density of 0.958
6 g/cc.

7 Example 10 - Polymerization - Catalyst F

8 Polymerization was performed as in Example 7 except that .500
9 grams of Catalyst F was substituted for Catalyst D. 8.1 grams of
10 polyethylene was recovered having a molecular weight of 137,000 and a
11 density of 0.960 g/cc.

CLAIMS:

1. An olefin polymerization supported catalyst comprising the reaction product of at least one metallocene of a metal of Group 4b, 5b, and 6b of the Periodic Table and an alumoxane said reaction product formed in the presence of a support.
2. The olefin polymerization supported catalyst in accordance with claim 1 wherein the support is a porous inorganic metal oxide of a Group 2a, 3a, 4a or 4b metal.
3. The olefin polymerization supported catalyst in accordance with claim 2 wherein the support is silica.
4. The olefin polymerization supported catalyst in accordance with any of claims 1 to 3 wherein the metallocene is selected from titanium, zirconium, hafnium, and vanadium metallocenes and mixtures thereof.
5. The olefin polymerization supported catalyst in accordance with any of claims 1 to 4, wherein the alumoxane is methyl alumoxane.
6. The olefin polymerization supported catalyst in accordance with any of claims 1 to 5 wherein the aluminium to transition metal ratio in the supported product is in the range of 100:1 to 1:1 on a molar basis.
7. The olefin polymerization supported catalyst in accordance with claim 6 wherein the molar ratio is in the range of 50:1 to 5:1.
8. The olefin polymerization supported catalyst in accordance with claim 1 wherein the metallocenes are represented by the formulas



wherein Cp is a cyclopentadienyl ring, M is a Group 4b, 5b, or 6b transition metal, R is a hydrocarbyl group or hydrocarboxy having from 1 to 20 carbon atoms, X is a halogen, $m=1-3$, $n=0-3$, $q=0-3$ and the sum of $m + n + q$ is equal to the oxidation state of M, $(\text{C}_5\text{R}'_k)$ is a cyclopentadienyl or a substituted cyclopentadienyl; each R' is the same or different and is hydrogen or a hydrocarbyl radical selected from alkyl, alkenyl aryl, alkylaryl or arylalkyl radicals containing from 1 to 20 carbon atoms, or a link between two carbon atoms joined together to form a $\text{C}_4\text{-C}_6$ ring, R'' is a $\text{C}_1\text{-C}_4$ alkylene radical, a dialkyl germanium or silicon or an alkyl phosphine or amine radical bridging two $(\text{C}_5\text{R}'_k)$ rings; Q is a hydrocarbyl radical selected from aryl, alkyl, alkenyl, alkylaryl, or arylalkyl radicals having from 1-20 carbon atoms, hydrocarboxy radical having from 1-20 carbon atoms or halogen and each Q can be the same or different from each other; Q' is an alkylidene radical having from 1 to about 20 carbon atoms; s is 0 or 1; g is 0, 1, or 2; s is 0 when g is 0; k is 4 when s is 1 and k is 5 when s is 0.

9. The olefin polymerization supported catalyst in accordance with claim 8 wherein the metallocenes are selected from bis(cyclopentadienyl) zirconium dichloride, bis(cyclopentadienyl) zirconium methyl chloride, bis(cyclopentadienyl) zirconium dimethyl, bis(methylcyclopentadienyl) zirconium dichloride, bis(methylcyclopentadienyl) zirconium methyl chloride, bis(methylcyclopentadienyl) zirconium dimethyl, bis(pentamethylcyclopentadienyl) zirconium dichloride, bis(pentamethylcyclopentadienyl) zirconium methyl chloride, bis(pentamethylcyclopentadienyl) zirconium dimethyl, bis(n-butyl-cyclopentadienyl) zirconium dichloride, bis(n-butylcyclopentadienyl) zirconium methyl chloride, bis(n-butyl-cyclopentadienyl) zirconium dimethyl, bis(cyclopentadienyl) titanium diphenyl, bis(cyclopentadienyl) titanium dichloride, bis(cyclopentadienyl) titanium methyl chloride, bis(cyclopentadienyl) titanium dimethyl, bis(methylcyclopentadienyl) titanium

diphenyl, bis(methylcyclopentadienyl) titanium dichloride, bis(methylcyclopentadienyl)- titanium diphenyl, bis(methylcyclopentadienyl)- titanium methyl chloride, bis(methylcyclopentadienyl)titanium dimethyl, bis(pentamethylcyclopentadienyl)titanium dichloride, bis(pentamethylcyclopentadienyl)titanium diphenyl, bis(pentamethylcyclopentadienyl)titanium methyl chloride, bis(pentamethylcyclopentadienyl)titanium dimethyl, bis(n-butyl-cyclopentadienyl)titanium diphenyl, bis(n-butyl-cyclopentadienyl)titanium dichloride and mixtures thereof.

(10. A method for preparing an olefin polymerization supported catalyst comprising a support and the reaction product of at least one metallocene of a metal of Group 4b, 5b and 6b of the Periodic Table and an alumoxane, comprising adding to a slurry of the support in an inert hydrocarbon solvent an alumoxane in an inert hydrocarbon solvent and a metallocene.

(11. A method for preparing polymers of ethylene or copolymers of ethylene and alpha olefins or diolefins said method comprising effecting the polymerization in the presence of the olefin polymerization catalyst of any of claims 1 to 9.



European Patent
Office

EUROPEAN SEARCH REPORT

0206794

Application number

EP 86 30 4806

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, A	EP-A-0 128 045 (EXXON) * Claims; page 9, lines 26-31 *	1	C 08 F 4/76 C 08 F 10/00
D, A	EP-A-0 035 242 (SINN HANSJÖRG) * Claims *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22-09-1986	Examiner DE ROECK R.G.
CATEGORY OF CITED DOCUMENTS			
X particularly relevant if taken alone Y particularly relevant if combined with another document of the same category A technological background O non-written disclosure P intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons B : member of the same patent family, corresponding document	